

EXAFS Studies of Mo, Ni-Y-Zeolite Catalysts

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Introduction

Bimetallic zeolite catalysts which contain Mo are of great interest as bifunctional catalysts¹⁻⁴. However, there are difficulties in preparing such catalysts since it is difficult to exchange the cations of a zeolite for molybdenum ions directly because high valence cationic molybdenum can only exist in a very acidic solution where ion-exchange equilibria are unfavorable and many zeolites are unstable. Ion exchange with neutral and anionic species results in a large amount of surface loading. In order to overcome the difficulties of aqueous ion exchange, molybdenum is introduced into zeolites by a solid-ion exchange method. A special procedure was developed recently for initiating controlled immigration of $\text{MoO}_2(\text{OH})_2$ into the pores of HY and NiY using MoO_3 in the presence of water vapor.⁵

EXAFS is an effective physical method for determination of the local structure of specific atoms in complex systems such as highly dispersed supported metal catalysts. It has been successfully applied to some metal zeolite catalysts: viz. Pt-Y-zeolite⁶, Cd-Y-zeolite⁷ and Ni, Mo-Y-zeolite⁸ and other bimetallic catalysts⁹⁻¹⁰. In this work, we studied by EXAFS the change of the environment around Mo and Ni as a function of preparation of the Mo, Ni-Y-zeolite to follow the incorporation of Mo and Ni into the framework of the Y-zeolite and to see if there are any Mo-Ni interactions.

Experimental

Samples

The HNaY was prepared by exchange of NaY with a 0.1 N NH_4NO_3 solution at 365K for 1 hour, followed by a direct calcination at 823K for 5.5 hours in a closed vessel. The modified solid ion exchange was performed as following: a mixture of 27 g HNaY and 1.2g MoO_3 was ground in a mortar (hereafter denoted as MoHY), placed in a quartz tube and then calcined at 723K, water vapor at 323K (118 torr) was carried through the mixture using H_2 as vector gas with a flow of 45ml/min. The sample obtained after calcination was then denoted as MoHYR and that after dehydration at 673K as MoHYRD.

The NiY was prepared by ion exchange of HNaY in a 0.5N $\text{Ni}(\text{NO}_3)_2$ solution at 318K for 3.5 hours, followed by washing and drying at 393K. To prepare one bimetallic catalyst, MoHYRD was subjected to the same ion exchange process in $\text{Ni}(\text{NO}_3)_2$ solution. This sample was denoted as MoNiY (Mo 1.63 wt. %, Ni 2.09 wt. %). A second sample was prepared starting with NiY and using solid ion exchange to incorporate Mo. This sample is denoted NiMoY (Ni 2.07%, Mo 2.5%). After dehydration they are denoted as MoNiYD and NiMoYD respectively. The Mo and Ni contents of the samples were then analyzed by AAS and Na contents were determined by ICP, and X-ray powder diffraction measurements were made using a Cu-target x-ray tube.

X-ray Absorption Measurements

X-ray absorption experiments were performed on beam line X-11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The X-ray absorption spectra for Mo and Ni K-edges were recorded with the ring operating at 2.5 GeV beam energy and a beam current of 40-180 mA. The pressed powder samples were mounted on the holder and measured at liquid nitrogen temperature in the transmission mode.

Data analysis was carried out with using standard methods¹¹ and the fitting was done using experimentally determined Mo-O (from ZnMoO_4), Mo-Mo (from metallic Mo) and theoretically calculated Mo-Si, Mo-Ni, Ni-Si, Ni-O and Ni-Ni (using FEFF)¹² phase shifts and backscattering amplitudes. Both single or multiple shell models were assumed for fitting the various filtered Fourier transform (FT) peaks.

Results and Discussion

Mo in Mo,Ni-Y-zeolites

As mentioned above, two different preparations were used: one put Mo into the zeolite first using solid-ion exchange and then introduces Ni cations by aqueous ion exchange. The other incorporates Ni first followed by Mo. Will the different order of incorporating Mo and Ni into Y-zeolite produce different local environments of Mo and Ni in these two catalysts? For these low loading and highly dispersed metal-zeolites, only EXAFS studies of the individual metal elements in them can give the answer to this question.

From Fig.1 it can be seen that the X-ray absorption profile of Mo in NiMoY and NiMoYD in which Mo was introduced into Ni-Y-zeolite are similar to those in MoO_3 and MoHY⁷ having a clear pre-edge peak and the weak structure in the extended absorption region. The spectra of Mo in MoNiY and MoNiYD are virtually the same as those in MoHYR and MoHYRD⁷: no pre-

edge absorption and with a strong oscillation in the extended region which means prominent higher coordination shells.

Fourier transforms of $k^3 \cdot \chi(k)$ for the Mo K-edge EXAFS of figure 1 shows that these differences are in both the first and higher shells (Fig.2). The Mo environment in NiMoY is very similar to MoO₃. The clear decrease of a Mo-Mo feature and a longer Mo-O distance in NiMoYD, in comparison with NiMoY indicates that MoO₃ is further dispersed into the Ni-Y zeolite by the further calcination and dehydration. This is also consistent with the decrease in the higher (Mo-Mo and Mo-O) shells. The fitting results listed in Table 1 quantitatively demonstrate these changes. For both MoNiY and MoNiYD, where Mo was introduced into Y-zeolite by solid-ion exchange, the higher coordination shell structures surrounding Mo are similar and sharper than those in NiMoY and NiMoYD. It is also known that the infrared absorption spectra are nearly same for both MoNiY and MoNiYD.⁷ The long metal oxygen bonds at around 2.6Å in both MoNiY and NiMoY (see Table 2) have been observed before in metal-zeolites.¹³ A Mo-Mo interaction ($R \sim 3.63$ Å) also was observed by EXAFS in MoO₃/TiO₂ catalysts after calcination.¹⁴ From fitting the experimental $k^3 \chi(k)$ data for MoNiY and MoNiYD isolated from the shells between 2.86 and 3.74Å with Mo-Mo, Mo-Si and Mo-Ni models it can be demonstrated that the Mo has not only Mo and Si which are present in MoHYR and MoHYRD but also a small amount of Ni atoms as its neighbors. An example is shown in Figure 3 for the case of MoNiY. The presence of an interaction between Mo and Ni in Mo,Ni-Y-zeolites may be significant for the catalytic properties of these bimetallic zeolite catalysts.

Ni in Mo,Ni-Y-zeolites

The Ni K-edge absorptions for MoNiY, MoNiYD, NiMoY and NiMoYD all have a strong first X-ray absorption peak which can be related to the oxidation state of Ni (see Fig.4). However, further comparison indicates that there are slight differences in the edge region and a great change in the extended region between MoNiY and NiMoY in both the as-prepared and dehydrated forms. The Fourier transforms of the data in Figure 4 are shown in Figure 5 and clearly show the differences between the MoNi and NiMo forms. The local environment of Ni in MoNiY is very close to that of dispersed NiO (CN=6, $R=2.04$ Å). After dehydration, the oxygen coordination decreases because of the removal of bound waters, and the Debye-Waller factor decreases. However, the higher shell coordinations still could not be found. Ni²⁺ is still present in a highly dispersed state with a simple oxygen coordination structure only. This is in agreement with other work.¹⁵ The strong interaction between Mo and Ni, as indicated in the previous paragraph, will inhibit the growth of Ni metal particles and results in the

fine Ni particles which would relate to excellent activity and selectivity toward hydrodemethylation of toluene.¹³ In NiMoY and NiMoYD the Ni-O first neighbors have overlapping contributions from higher shells. Multiple shell fitting showed that best fits were obtained for Ni-O, Ni-Si and Ni-Ni coordinations compared with those for Ni-O and Ni-Si or Ni-O and Ni-Ni only. An example of the results with Mo, Ni and O as the neighbors fitted to Fourier filtered data between 2.86-3.74 Å in NiMoY is shown in Figure 6. It indicates that Ni has not only O and Ni but also Mo as its coordination neighbors consistent with the Mo edge results on the same samples.

Summary

From Mo and Ni K-edge EXAFS studies we have studied the difference between the local environments of Mo and Ni in Mo,Ni-Y-zeolites prepared by interchanging the order of introduction of metals into the zeolite. The results clearly indicate that significant differences occur. When Mo is introduced first it seems to be exchanged into the supercages as indicated by the coordination numbers and distances we have found. The subsequent addition of Ni seems to allow Ni to go into nearby cages where it can coordinate to Mo through oxygens. When Ni is added first it seems to go into a smaller cages in an aqueous phase. Subsequent addition of Mo does not affect this environment and the Mo seem to remain essentially as MoO₃. This should not result in an effective interaction between Mo and Ni. These results clearly indicate the importance of the order of exchange of metals onto zeolites in the preparation of bimetallic zeolite catalysts.

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Table 1 Mo Coordination Shells in Mo,Ni-Y-Zeolites

MoNiY					MoNiYD				
Model	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	
Mo-O	3.2±.2	2.03±.01	0.01±.00	-4.3±.6	2.2±.2	2.00±.01	-0.27±.02	-1.1±.1	
Mo-O	1.4±.1	2.62±.01	-0.69±.06	-7.6±.7	0.7±.1	2.61±.01	-0.77±.04	8.4±.6	
Mo-Ni	0.9±.2	3.54±.01	0.40±.03	7.1±.6	0.1±.0	3.63±.02	-0.83±.05	7.0±.6	
Mo-Mo	3.4±.1	3.70±.02	-0.14±.01	6.1±.4	3.6±.3	3.68±.02	-0.05±.02	6.0±.4	
Mo-Si	1.5±.1	4.05±.02	-0.02±.02	-3.0±.3	1.0±.1	4.00±.02	-0.40±.03	3.3±.3	
NiMoY					NiMoYD				
Model	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	
Mo=O	0.5±.1;	1.55±.01	-0.03±.01	13.5±3.	0.1±.0	1.53±.01	-0.37±.02	11.7±.9	
Mo-O	3.2±.3	1.71±.01	0.04±.01	6.8±.7	2.3±.2	1.72±.01	-0.06±.01	6.8±.6	
Mo-O	1.2±.2	1.98±.01	-0.48±.02	-12.6±.8					
Mo-Mo	2.2±.4	3.31±.01	-0.03±.01	3.7±.3					

Table 2 Ni Coordination Shells in Mo,Ni-Y-Zeolites

NiMoY					NiMoYD				
Model	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	
Ni-O	4.3±.2	2.08±.01	0.01±.01	-0.6±.3	4.1±.3	2.07±.01	0.13±.01	2.4±.3	
Ni-Si	2.7±.2	2.68±.01	0.22±.01	12.8±.9	1.9±.2	2.66±.01	0.10±.01	14.3±.9	
Ni-Ni	2.3±.1	3.03±.01	0.77±.01	-1.2±.5	2.9±.2	2.98±.01	0.72±.04	5.5±.5	
Ni-Ni	1.8±.1	3.94±.01	0.42±.01	8.2±.7	2.1±.2	3.96±.01	0.40±.01	3.9±.4	
Ni-Mo	4.0±.4	4.51±.02	0.72±.01	14.2±1.	4.0±.3	4.53±.02	0.70±.08	15.0±1.2	
Ni-O	2.1±.2	4.95±.02	-0.91±.01	-9.6±.3	2.9±.4	4.97±.02	-0.78±.0	-11.3±.4	
MoNiY					MoNiYD				
Model	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	CN	R(Å)	DWF.10 ²	d-E ₀ (eV)	
Ni-O	4.9±.2	2.04±.01	0.36±.01	6.5±.4.	3.2±.3	2.05±.01	-0.13±.01	9.3±.4	

Note: The experimental standard data are used for fitting: Mo-O(CN=4,R=1.78) from ZnMoO₄ and Mo-Mo (CN=12,R=2.73Å) from Mo metal foil; FEFF program was used to calculate the standard data for Mo-Si(CN=12, R=2.69Å), Mo-Ni(CN=12, R=2.61Å), Ni-O(CN=6,R=2.09Å), Ni-Si(CN=12,R=2.69Å), Ni-Ni(CN=12,R=2.96Å) and Ni-Mo(CN=12, R=2.61Å).

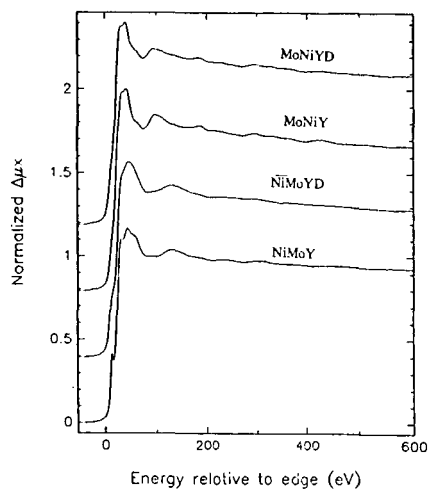


Fig.1 The normalized X-ray absorption spectrum versus energy for Mo in MoNiYD and MoNiY in which Mo were introduced first and in NiMoYD and NiMoY where Ni first. The energy scale is relative to the binding energy of the Mo 1s state (20,000 eV).

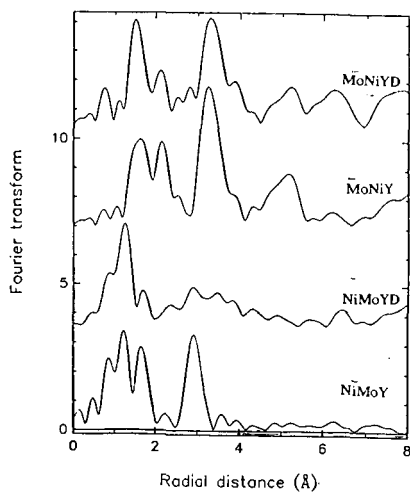


Fig.2 A comparison of the magnitudes of the Fourier transforms of the weighted Mo EXAFS for MoNiYD, MoNiY, NiMoYD and NiMoY zeolites versus R. The transforms are all of $k^3X(k)$ and taken over a k -space range of $3\text{--}14 \text{ \AA}^{-1}$.

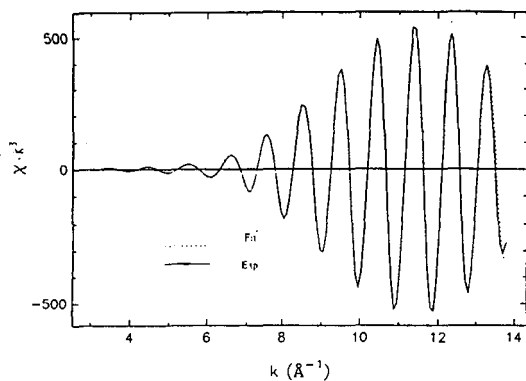


Fig.3 An overplot of the Fourier filtered $k^3X(k)$ data of Mo in MoNiY and the best fitting results (see Table 1) versus R . The fitting range was from 2.86 to 3.74Å. The fit included Mo-Mo, Mo-Ni and Mo-Si contributions.

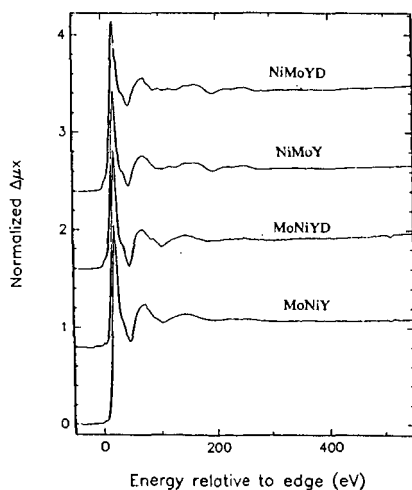


Fig.4 The normalized X-ray absorption spectrum versus energy for Ni in NiMoYD and NiMoY in which Ni were introduced first and in MoNiYD and MoNiY where Mo first. The energy scale is relative to the binding energy of the Ni 1s state.

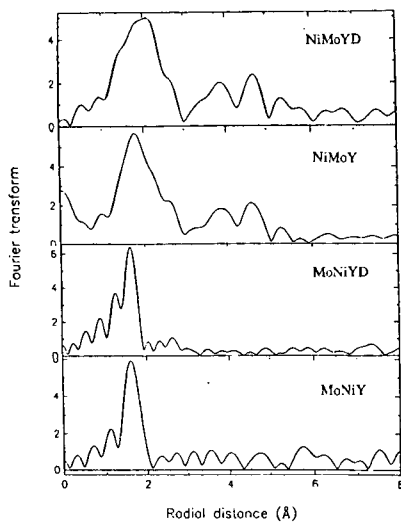


Fig.5 A comparison of the magnitudes of the Fourier transforms of the weighted Ni EXAFS for NiMoYD, NiMoY, MoNiYD and MoNiY zeolites versus R. The transforms are all of $k^3X(k)$ and taken over a k -space range of $3\text{--}14 \text{ \AA}^{-1}$.

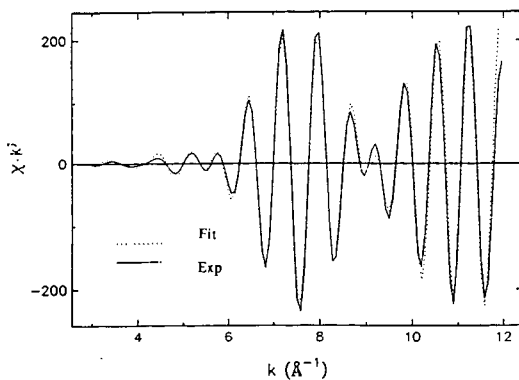


Fig.6 An overlplot of the Fourier filtered $k^3X(k)$ data of Ni in NiMoY and the best fitting results (see Table 2) versus k . The fitting range was from 3.0 to 5.1 \AA . The fit included Ni-Ni, Ni-Mo and Ni-O contributions.